

Blends of Cellulosic Esters with Poly(caprolactone): Characterization by DSC, DMA, and WAXS

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SYNOPSIS

Binary blends of poly(caprolactone) (PCL) with cellulosic esters [cellulose diacetate (CDA), cellulose acetate–butyrate (CAB), and cellulose triacetate (CTA)] were studied by using differential scanning calorimetry (DSC), dynamic mechanical analysis (DMA), and wide-angle X-ray scattering (WAXS) techniques, and qualitative comparison was made with the results obtained by polarizing optical microscopy. The PCL–CAB system was proved to be partially miscible, whereas PCL–CDA and PCL–CTA appeared to be immiscible. A double-melting behavior was showed for PCL–CAB and PCL–CTA blends. As these peaks did not shift by varying the heating rate of DSC runs, this behavior can be due to melting of two populations of crystals of PCL, which may be different in size. On the other hand, blends of PCL containing a low amount of CAB or CDA seem to develop more crystallinity for the PCL than this polymer alone. The solvent seems to have a certain influence on the thermal and morphological behaviors of the as-cast blends of these three systems, affecting the extent of crystallinity of PCL, as well as its T_m and ΔH_f . This finding is discussed in the light of WAXS and polarizing optical microscopy results. © 1994 John Wiley & Sons, Inc.

INTRODUCTION

Polymer blends have shown to be an excellent way for developing new materials often exhibiting combinations of properties superior to either of the pure components alone. Due to the technological importance of these materials, many fundamental studies have been devoted to miscibility of polymeric systems. Although a number of immiscible blends are of technological importance, miscible blends have received special attention. This is because miscible and partially miscible blends represent a good opportunity for knowledge about the thermodynamic aspects of interacting groups, which are often responsible for miscibility in these systems. A major number of miscibility studies on polymer systems

has been devoted to amorphous polymers. However, in recent years, there has been a steadily growing interest, expressed from both the academic and industrial communities, on compatible systems having at least one crystallizable component. This is partially due to the fact that one-half to two-thirds of all commercially significant polymers are crystalline or crystallizable. Therefore, modification of crystallizable polymers by blending them with either amorphous or other crystallizable polymers is a very promising way to obtain a diversity of new materials.

A well-known example of miscible blends involving a semicrystalline polymer is that of poly(ϵ -caprolactone) (PCL) with poly(vinyl chloride) (PVC).^{1,2} PCL is also miscible with several polymers such as poly(hydroxyether of bisphenol-A)³ and copolymers of styrene containing either maleic anhydride⁴ or acrylonitrile,⁵ among others. The driving force for miscibility in these systems has been attributed to hydrogen bonds between groups of both components.

On the other hand, some cellulosic derivatives

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(CDs) contain high concentration of hydroxyls quite amenable for specific interaction throughout hydrogen bonds, as pointed out elsewhere⁶ for cellulosic esters. In these interactions the nonsubstituted hydroxyls behave as the proton-donor groups and the carbonyls of the ester groups behave as the proton-acceptor groups. In this line of thought, polymers containing carbonyls or highly polar groups may interact with CDs giving miscible blends, providing that the enthalpy associated with such interactions is higher in value than that of interactions occurring in pure CDs. This condition appears to be present only in a low number of blends in which a CD is one of the components. As a consequence, studies on such blends are scarce in the literature,⁶ in spite of the technological importance of CDs. For example, phosphorylated poly(styrene) and phosphorylated poly(2,6-dimethyl-1,4-phenylene oxide) were claimed to be miscible with a series of CDs including cellulose diacetate (CDA), cellulose acetate-butyrate (CAB), cellulose butyrate, and nitrocellulose.⁷ Cellulose nitrate gives miscible blends with PCL^{8,9} and with poly(methyl acrylate) (PMA),¹⁰ among others. CAB is also partially miscible with ethylene-co-vinyl acetate copolymer¹¹ and with PCL at intermediate concentrations.⁹ However, from our point of view, there are some thermal and morphological aspects shown by the PCL-CAB system that require more detailed studies.

In this work, results of studies carried out on binary blends of PCL with cellulose triacetate (CTA), CDA, and CAB, by using differential scanning calorimetry (DSC) and dynamic mechanical analysis (DMA), are reported. With basis on the DSC and DMA results, a PCL-CAB blend is proved to be partially miscible, whereas blends of PCL with CDA and CTA are immiscible. ¹³C-NMR spectroscopy was used for checking a possible transesterification and/or decomposition of pure PCL, CAB, and their blends. The thermal behavior of these three systems are discussed in the light of results obtained by applying wide-angle X-ray scattering (WAXS) and polarizing optical microscopy (POM).

EXPERIMENTAL

Materials

All polymers used were purchased from Polysciences, Inc. (USA): CTA (Cat. #4078), CDA (acetyl content 39%, Cat. #6203), CAB (butyryl content 17%, Cat. #6206), and PCL (Cat. #7039, M_w of 35,000–45,000). Unfortunately, the supplier does not give information about molecular weights for the cellulosic esters. However, judging from the infor-

mation provided by other suppliers for these polymers, their molecular weights (M_w) are expected to range from 30,000 to 42,000. Reagent-grade acetone and dichloromethane were acquired from Merck (México). All these polymers and solvents were used as received.

Blends Preparation

Polymers to be mixed were allowed to dissolve separately at room temperature in the appropriate solvent. Dichloromethane was used for blends of CTA and CAB, while a mixture of dichloromethane/acetone (70/30) was used for blends with CDA. The resulting solutions, with 2% by weight of polymers, were mixed together and stirred with a magnetic bar at room temperature for 1 h. Films of the polymer blends were obtained by casting these solutions after pouring into petri dishes and allowing the solvent to evaporate at room temperature. These films were dried in a vacuum oven for 48 h at 80°C. Samples to be tested on DMA were prepared by mixing the respective homopolymer solutions and casting the resulting mixtures at room temperature and slow evaporation of solvent. Residual solvent was eliminated by allow the blends to stand at 80°C in a vacuum oven for 1 week. Then, these samples were pressed between two glass plates and put into a vacuum oven at 150°C for 30 min to have sheets of homogeneous thickness. Rectangular samples (40 × 10 mm²), 0.8–1.0 mm of thickness, were cut from the obtained sheets of blends and pure cellulosic derivatives.

Blends Characterization

Samples (25–30 mg) of blend films were tested by duplicate and using a Perkin-Elmer DSC-2C calorimeter. Standard aluminum sample pan holders (Perkin-Elmer) were used. Large samples were required because the signal at the glass transition temperature (T_g) of cellulose acetates is often of low intensity. Three consecutive DSC runs were carried out on each sample of pure and blended polymers. Heating and cooling rate was 10 K/min, from 213 to 515 K, under a N₂ flux of 20 cm³/min. DSC apparatus was previously calibrated with tin and indium following the usual procedure. Data acquisition was made with a 1600 Data Station (Perkin-Elmer) coupled with the DSC apparatus. Calculations were performed by using the TADS program (Perkin-Elmer). T_g was measured at the onset of DSC thermograms, while melting temperature (T_m) was taken at the maximum of endothermic

peak. DMA thermograms were obtained for PCL-CAB and PCL-CTA blends by using a DMA V4.2C (TA Instruments) apparatus. These runs were performed at 2000 Hz and oscillation amplitude of 0.300 mm. Heating was from -75 to 220°C and a heating rate of $5^{\circ}\text{C}/\text{min}$. ^{13}C -NMR spectroscopy was used to check whether transesterification or decomposition took place in PCL-CAB blends under the applied DSC heating conditions. Deuterated chloroform was used to dissolve the samples, and spectra were obtained with a Gemini 200 NMR apparatus.

WAXS studies were performed on blends by using a horizontal goniometer Philips (Model PW-1140/60), which was coupled with a $\text{CuK}\alpha$ target X-ray tube operated at 40 kV and 30 mA. Monochromatization was achieved by Bragg's diffraction from a graphite crystal. Diffraction intensity was recorded with a proportional counter coupled with a discriminator-integrator (Ratemeter) system; 2θ angle was scanned from 5° to 60° , at $1^{\circ}/\text{min}$. The areas (8 – 12 in.²) of diffractograms were measured by using a planimeter, and percent of apparent crystallinity (crystalline index) was evaluated from ratio of the areas of the crystalline peaks to the total area under the scattering curve.^{12,13} WAXS experiments were carried out by duplicate both on the as-cast samples, before the first DSC run was obtained, as well as on the heated and cooled back samples. Cooling and heating for this purpose were conducted at 10 K/min in the DSC apparatus. To assure that no preferential orientation took place in blends, WAXS diffractograms were also obtained for samples containing 50% of CDs with PCL, after rotation at 45° and 90° from the original position.

Blends morphology was observed with an optical microscope (Microscopios, S.A., México) under cross polarization, using an M40/0.65 objective in incident light. For these studies very thin films were obtained by casting two drops of polymer solutions (4 wt % of polymers) on microscope-glass cover slides, allowing them to dry at room temperature (22°C). Heating and cooling were carried out on hot stage plate (Leitz) at same rates as in DSC runs. Photomicrographs were obtained with a 35mm camera (Minolta), using a first-order red filter to get contrast between textural features on the microscopic image.

RESULTS AND DISCUSSION

PCL-CAB blends

Representative DSC thermograms (first and second runs) obtained for these blends are showed in Figure

1. As can be observed in this figure, T_g is not clearly resolved in the first-run curves for 50/50 and 25/75 blends, but it appears well defined in the second runs. It is worth mentioning that features of the second-run traces were reproduced on subsequent runs and that T_g was not clearly appreciated on DSC traces for blends containing amounts of CAB lower than 40% (not showed here), which may be due to the small value of ΔC_p at T_g for CAB. Nevertheless, T_g value in these blends (Fig. 1) clearly decreases with PCL content when compared to T_g of pure CAB. This dependence on composition is better appreciated on Figure 2, where T_g shows a steady decrease from 148°C for 100% CAB to about 114°C for blend containing 60% of PCL. As can be noted, T_g variation shows a nonlinear dependence on the blend composition, even though the composition in Figure 2 was corrected for the effective amorphous part of PCL. This correction was done by calculating the weight of the crystalline part of PCL, using the ratio of each experimental ΔH_f value to ΔH_u° ($= 32.4$ cal/g, the heat of fusion of 100% crystalline PCL that was measured from melting point depression of PCL by ethylbenzotate),¹⁴ and subtracting it from each nominal weight of this polymer blended with CAB. At this point, it is worth mentioning that these results apparently disagree with those reported by Hubbell and Cooper⁹ for PCL-CAB blends. However, it must be pointed out that these authors used a CAB having 1.2 butyryl and 1.0 acetyl groups per repeating unit, whereas the CAB used in this

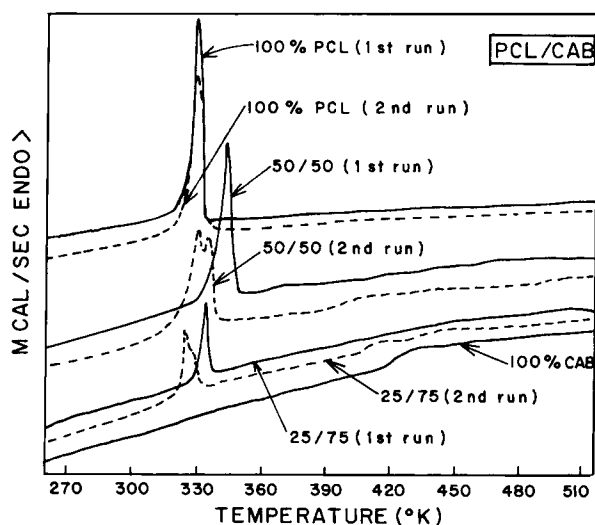


Figure 1 Representative DSC thermograms for PCL-CAB blends. Numerals indicate blend composition for traces obtained on (—) first runs and (-----) second runs. Experimental conditions: $10^{\circ}\text{C}/\text{min}$ under a N_2 flux of 20 cm^3/min .

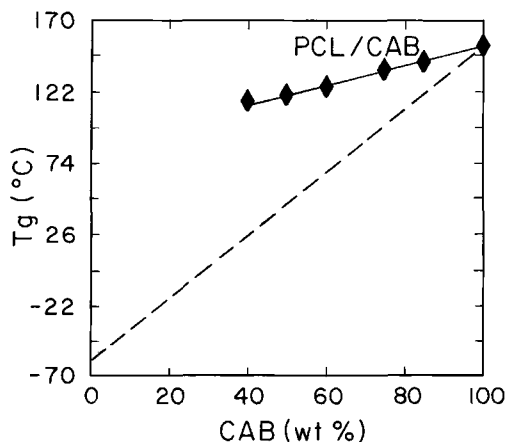


Figure 2 Glass transition temperature (T_g) as a function of composition for PCL–CAB blends. (◆) Experimental data and (---) estimated data by assuming a linear dependence of T_g blends with composition, as observed for typical miscible blends. Experimental error is indicated by the size of symbols in this and the following figures, in which curves were drawn only to indicate the trend of experimental data.

work contains 1.1 butyryl and 1.7 acetyl groups per repeating unit. T_g for the former one was reported to be of 48°C, whereas the later one showed a T_g of 148°C, as mentioned above. This difference in T_g is reasonably expected because flexibility is higher in butyryl than in acetyl groups, giving a lower T_g for the CAB containing a higher number butyryl groups. Hubbell and Cooper⁹ reported a range of –58 to –25°C for T_g of blends containing 25–80% of CAB, showing a nonlinear behavior with composition. Such a behavior was similar to that shown in Figure 2, though this takes place in a narrower range of composition and in the CAB-rich blends.

There are some additional interesting differences between curves in Figure 1. So, a well-defined double-melting peak can be appreciated on the second-run trace for a 50/50 PCL–CAB blend, while in the 25/75 blend the second peak appears just as a shoulder. As discussed elsewhere,¹⁵ the double-melting behavior of polymers in DSC experiments may be due to: (i) recrystallization effect, which arises from melting of imperfect crystals, followed by recrystallization into less imperfect crystals and then final melting; (ii) morphological effect, which implies melting of two populations of crystals, differing in both size and thickness, which will melt at two different temperatures. Melting peak at higher temperature corresponds to less imperfect crystals formed through primary crystallization of PCL, while that at lower temperature belongs to more imperfect crystal formed from secondary crystalliza-

tion. This later process takes place in amorphous regions containing both components, to which the noncrystallizable polymer migrates during the primary crystallization process.¹⁵ Although kinetic effects might be present at relatively low heating rates, and the addressing of double-melting would be therefore a rather complex task,^{15,16} the foregoing effects can be distinguished by varying the heating rate in DSC runs. Accordingly, the position of peaks depends on the heating rate for the recrystallization effect, whereas this position is independent on heating rate for the morphological effect. Double-melting endotherms has been reported for polyethylene¹⁷ and poly(ether ether ketone),¹⁸ among others, and has been explained as a result of recrystallization effect. On the other hand, the double-melting behavior observed for miscible blends of PCL with poly(hydroxy ether of bisphenol-A),³ styrene-co-maleic anhydride copolymers,⁴ and poly(styrene-co-acrylonitrile)⁵ has been ascribed to morphological effect (two populations of crystals). The lower T_m peak was attributed to secondary crystallization, which occurs after segregation of CAB out from the growing spherulites (primary crystallization process). Thus, to address the similar behavior observed in PCL–CAB blends, we performed DSC runs on small samples (0.5–3.0 mg) at 2.5, 5, 10, 20, and 60°C/min. Position of endothermal peaks remains the same for each heating rate for the blends containing 25 and 50% of CAB. Therefore, based on this criterion, it is indicative of the occurrence of two populations of crystals in these blends, though this needs to be directly confirmed by detailed small-angle X-ray scattering (SAXS) studies. Some morphological features will be qualitatively discussed below based on results obtained by POM. At present, this behavior is under study in more detail by SAXS and WAXS on PCL–CAB system at intermediate composition.

Regarding the endothermic peaks position (melting temperature, T_m) for PCL–CAB, as depicted in Figure 3, it is noteworthy that the T_m for blends with a relatively low content of CAB (up to 50% in the first run and 25% in the second run) is greater than that for pure PCL. The same effect can be observed in ΔH_f . This unexpected behavior of T_m and ΔH_f for blends containing a crystalline polymer is a very uncommon phenomenon that has been observed at least for two systems: poly(1,4-cyclohexanedimethanol terephthalate) with poly(carbonate of bisphenol-A)¹⁹ and for poly(vinylidene fluoride) with poly(vinyl acetate).²⁰ These blends seem to develop more crystallinity for crystallizable component than this polymer alone. Such a behavior

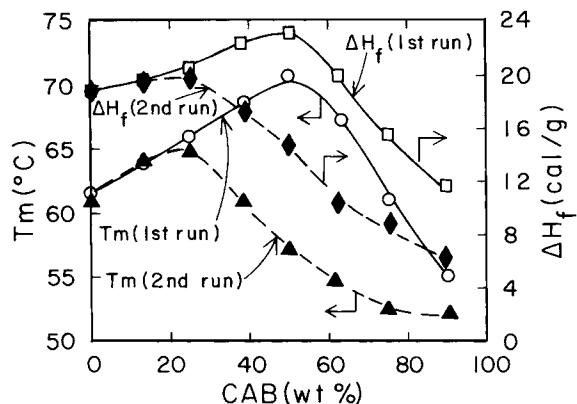


Figure 3 Thermal events for PCL-CAB blends as a function of composition. Melting temperature (T_m) on the (—○—) first and (---▲---) the second DSC runs. Enthalpy of fusion (ΔH_f) for the (—□—) first and (---◆---) the second DSC runs.

appears to be in disagreement with models for melting point depression for miscible or partially miscible blends. Speculatively, this anomalous behavior has been associated with thickening of lamellae,²⁰ which seems to be reasonable because polymer viscosity of mixtures increases slowly as the solvent evaporates on a casting process. As a consequence, chains of crystallizable polymer would have enough time to crystallize in well-defined lamellae. The small increase in apparent crystallinity observed only for the as-cast films in this blend region (upper part of Fig. 5, continuous curve) seems to concur roughly with this hypothesis. However, it remains to be understood why the samples containing 25% of CAB, or lower, also exhibited this anomalous behavior on second DSC runs, despite that the solvent history was previously removed after the first run. Thus, detailed characterization of size and thickness of lamellae is needed to confirm or refuse the morphological origin of this phenomenon.

For intermediate and higher contents of CAB, an increase in composition of this polymer causes a decrease on T_m , about 9 K from 50 to 75 wt % CAB in the first run, and about 11 K from 25 to 75 wt % CAB in the second run. Also, by comparison of second- and first-run traces for each composition, a drastic decrease of T_m is observed for blends with composition of CAB higher than 25% (Fig. 3), being the highest decrease that of the 50/50 blend. A similar behavior is showed by melting enthalpy (ΔH_f) versus blend composition in a narrower composition range. This behavior was also observed elsewhere²¹ for nylon 6-PCL blends. It must be emphasized that all the ΔH_f data reported in Figure 3 were normalized with respect to the content of PCL in each blend.

So, curves in Figure 3 indicate an actual decay in ΔH_f values with blend composition. Otherwise, a horizontal line would fit these data. These results harmonize with the idea of partial miscibility for PCL-CAB blends in the composition range above 50% CAB, which becomes more evident in second-run DSC traces because solvent history was eliminated by heating during the previous first DSC runs. This fact agrees very well with WAXS experiments carried out on this blend, as discussed below.

Figure 4 reports representative thermograms of dynamic mechanical measurements for PCL-CAB blends. Figures 4(a), (b), and (c) correspond to pure CAB, 25/75, and 50/50% PCL-CAB blends, respectively. Pure CAB exhibits a peak on the tan

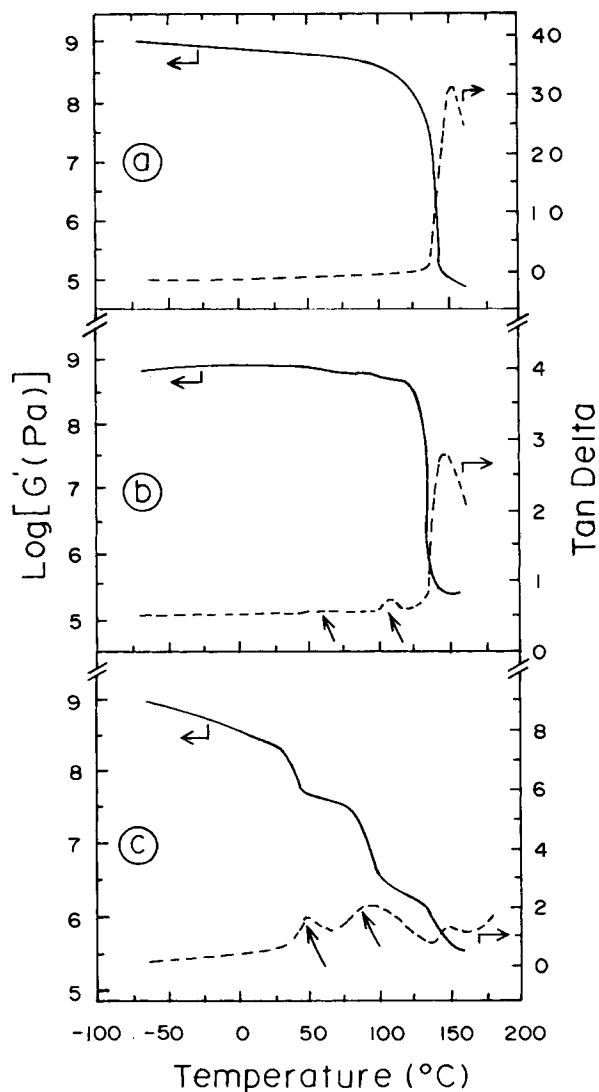


Figure 4 (—) Shear modulus G' and (---) tan delta from dynamic mechanical measurements: (a) pure CAB, (b) 25/75 PCL-CAB, and (c) 50/50 PCL-CAB.

delta curve with a maximum at 155°C [Fig. 4(a)], which is only 7°C higher than the T_g obtained from DSC measurements. Pure CAB also shows a drop in its shear modulus G' by about 3.5 decades in the temperature range 115–145°C. When CAB contains 25% PCL [Fig. 4(b)] two additional peaks of tan delta appear in the temperature ranges 50–60°C and 100–115°C, and the corresponding drops in the shear modulus G' at slightly lower temperature. Similar features are also shown by the 50/50 PCL–CAB blend [Fig. 4(c)], but the two additional peaks in tan delta curve appear broader and increased in size. In contrast, the peak observed in pure CAB slightly shifts to a lower temperature and notoriously becomes smaller. The corresponding drops in shear modulus G' are also enhanced in comparison to those of Figure 4(b) except that in 125–150°C. This is expected because the amount of PCL was increased.

From these observations, it can be inferred that the peak at about 50°C corresponds to melting of PCL crystals in blends. The extent of crystallization is higher for the blend containing 50% PCL than that of 25% PCL. These results qualitatively agree with the ΔH_f dependence on the PCL content (Fig. 3) and with the crystallinity index, as will be discussed below, for PCL–CAB blends. Furthermore, it is clear that the broad peak in the temperature range 75–125°C corresponds to glass–rubber transition, namely $T_{\alpha 1}$, for this blend, and decreases from about 105°C for 25% PCL to 90°C for 50% PCL. Moreover, the transition at higher temperature, $T_{\alpha 2}$, which decreases in size and remains in its original position with the PCL content, corresponds to the separate CAB. As expected, this peak tends to vanish for PCL-rich blends. Table I reports glass–rubber transition temperatures from DMA data. As can be observed in this table, $T_{\alpha 1}$ transition shows a non-linear dependence on composition. This finding clearly indicates that the PCL–CAB system is partially miscible and agrees with the above discussion

Table I Glass–Rubber Transition for PCL–CAB Blends from Dynamic Mechanical Measurements^a

Blend Composition	Blend					
	PCL-CAB	0/100	10/90	25/75	50/50	60/40
$T_{\alpha 1}$, °C	—	130	105	90	80	
$T_{\alpha 2}$, °C	155	152	152	148	?	

^a $T_{\alpha 1}$ and $T_{\alpha 2}$ are the glass–rubber transition temperature peaks observed in tan delta curves and correspond to blended polymers and to CAB remaining not well mixed with PCL in the system. We were unable to obtain reproducible DMA thermograms for higher contents than 60% PCL.

on DSC data. Furthermore, the broadening of the peak at 90°C [Fig. 4(c)] and of T_g by DSC (Fig. 1) may speculatively be associated with possible amorphous microdomains, differing in composition, in PCL–CAB blends. Also, the peak at 148°C in Figure 4(c) suggests that not all the CAB is closely associated with PCL in these blends, at least up to 50% of PCL. Thus, it seems interesting to characterize the morphology of this blend by scanning electron microscopy and to applied models based on DMA results²² to predict morphological features of these blends.

WAXS diffractograms for PCL–CAB blends are depicted in Figures 5 and 6. Crystallinity decreases slightly with PCL content in the as-cast blends (Fig. 5), which coincides with that observed on the corresponding DSC thermograms (ΔH_f of first run, Fig. 3). This is more clearly noticed in Figure 7 (upper part), in which the crystallinity index follows approximately a linear dependence on the PCL content (continuous curve). In contrast, a different situation took place after these samples were heated up to 237°C and cooled back to room temperature: All peaks on WAXS diffractograms became lower in intensity (Fig. 6), like endothermic peaks on DSC curves (ΔH_f of second run, Fig. 3) and a quite drastic reduction in crystallinity with CAB content was observed (upper part of Fig. 7, discontinuous curve). Interestingly, a similar drastic drop in ΔH_f was also reported for the mentioned PCL–styrene-*co*-acrylonitrile (PCL–S-*co*-AN) copolymer.⁴ This result can be reasonably explained by assuming that solvent restricts the interaction between components during casting. After thermal treatment, casting history is removed and each blend closely reaches its own thermodynamic state under these conditions. These results concur closely with the partial miscibility determined by DSC and DMA on PCL–CAB system.

It is worth noticing that peak at $2\theta = 21.6^\circ$ in WAXS diffractograms (Fig. 5) decreases in intensity with the CAB content. Thermal treatment on these blends causes quite a drastic decrease in intensity of peaks at 21.6° and 24.2° (Fig. 6) without significant peak broadening. According to the concept of paracrystals,²³ which has proved to be applicable to semicrystalline polymers, there are two kinds of crystal distortions. Distortions of the first kind are found in crystal lattices, where dimensions of the unit cell and the electron density distribution vary statistically about ideal equilibrium positions from cell to cell, but the long-range periodicity (order) is preserved. Distortions of the second kind are characterized by changes in lattice points in relation to

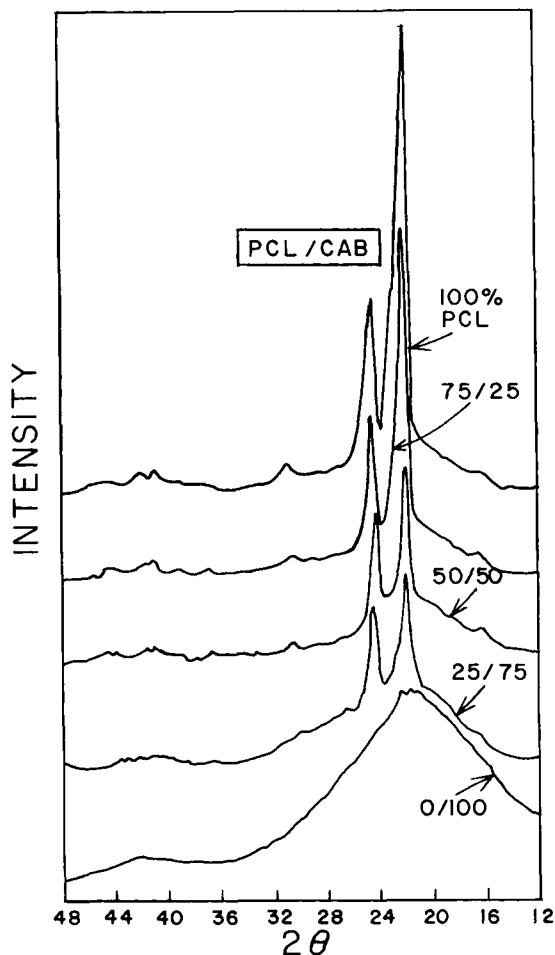


Figure 5 WAXS diffractograms for the as-cast PCL-CAB blends. Numerals on curves indicate blend composition.

their nearest neighbors, rather than to the ideal lattice points, resulting in the loss of long-range order. It has been shown²⁴ that distortions of the first kind cause a falling of intensity of peaks, but no broadening, of a series of reflections in WAXS profiles. Distortions of the second kind, in turn, result in both a diminishing intensity and an increase in the reflection breadth with the scattering angle.

From the above discussion, it seems reasonable to assume that the falling of intensity for peaks in WAXS diffractograms of PCL-CAB blends, particularly of those thermally treated samples (Fig. 6), is due to distortions of the first kind in PCL crystals. It must be emphasized that this is only a hypothesis that needs confirmation by a quantitative analysis of WAXS profiles, applying those equations derived from the concept of paracrystals.²⁴ Studies on blends of PCL with CAB and CTA are in progress to quan-

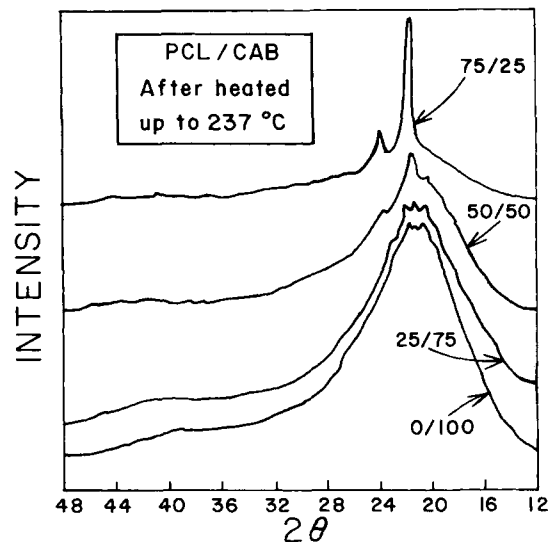


Figure 6 WAXS diffractograms for the PCL-CAB previously heated up to 237°C and cooled back to room temperature in the DSC apparatus. Heating and cooling rate was 10°C/min.

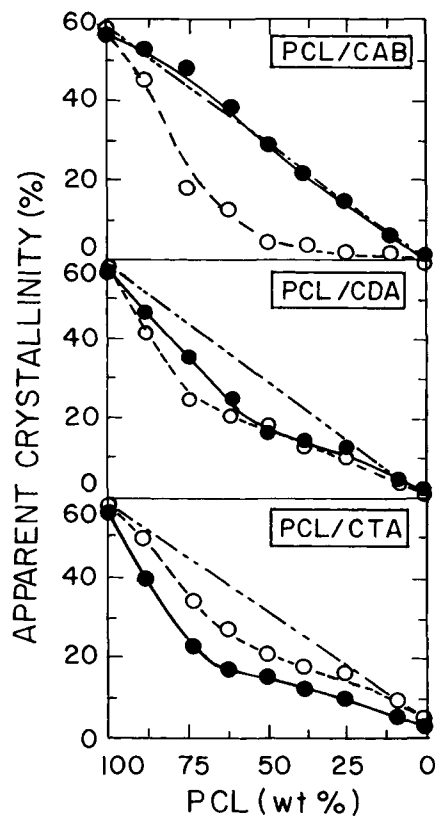
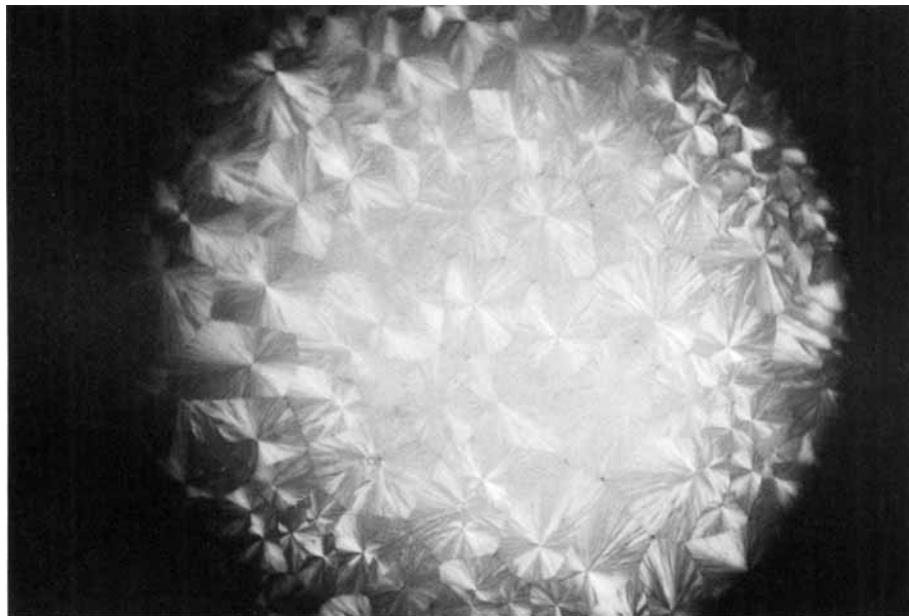


Figure 7 Percent of apparent crystallinity for PCL blends as a function of CD content: PCL-CAB (upper part), PCL-CDA (middle), and PCL-CTA (bottom part). For each case, curves correspond to the (●) as-cast blends, the (○) thermally treated blends, and the (---) estimated data by assuming the additivity rule for crystallinity of components in the blend.

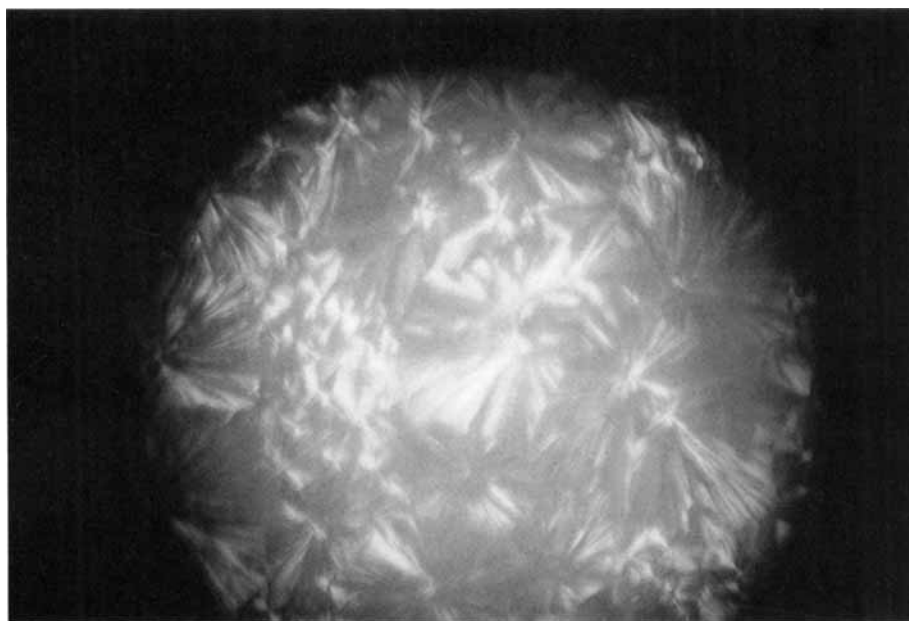
tify this possible distortion of the first kind in PCL crystals.

Photomicrographs obtained for PCL-CAB are shown in Figures 8(a) to 8(e). The as-cast PCL sample exhibits well-defined polygonal spherulites

[Fig. 8(a)] that are typical of those formed in terminated primary crystallization process of polymers.^{12,25} These spherulites suffered a distortion in shape as well as in size uniformity after heating [Fig. 8(b)]. Similar features are shown by the 75/25

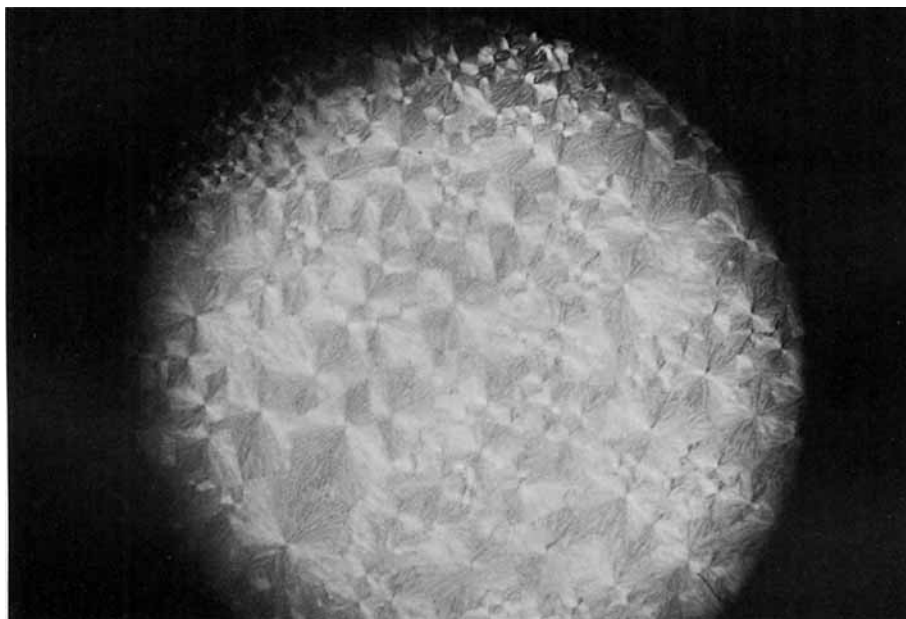


(A)

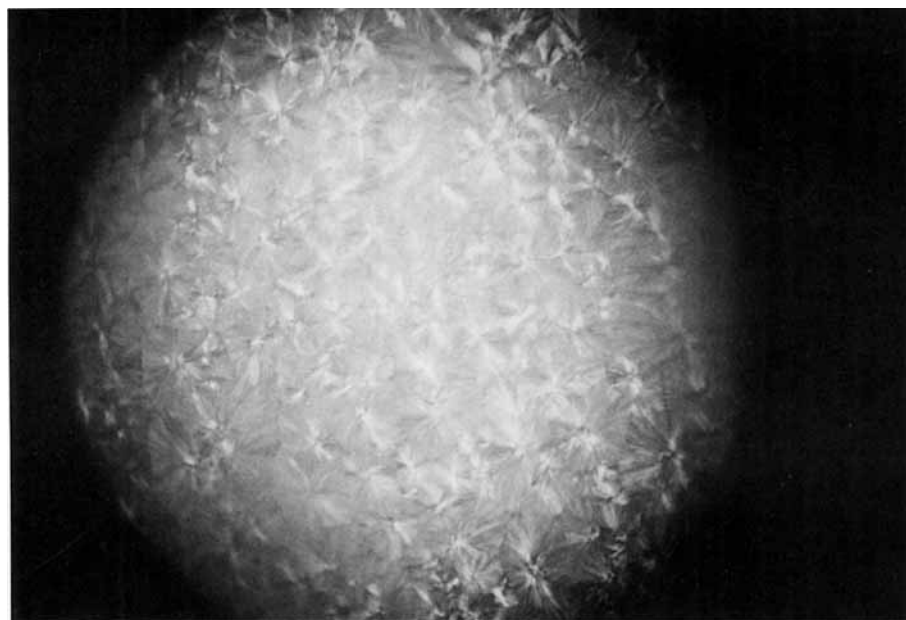


(B)

Figure 8 Polarized photomicrographs for PCL-CAB blends: (a) as-cast PCL showing polygonal spherulites and resembling those of the terminated primary crystallization process in polymers; (b) thermally treated PCL exhibiting a slight morphological distortion due to the heating-cooling cycle; (c) as-cast 75/25 (PCL-CAB) blend; (d) thermally treated 75/25 (PCL-CAB) blend; and (e) as-cast 25/75 (PCL-CAB) blend. These photomicrographs were obtained in incident light by using an M 40/0.65 objective and first-order red filter.



(C)

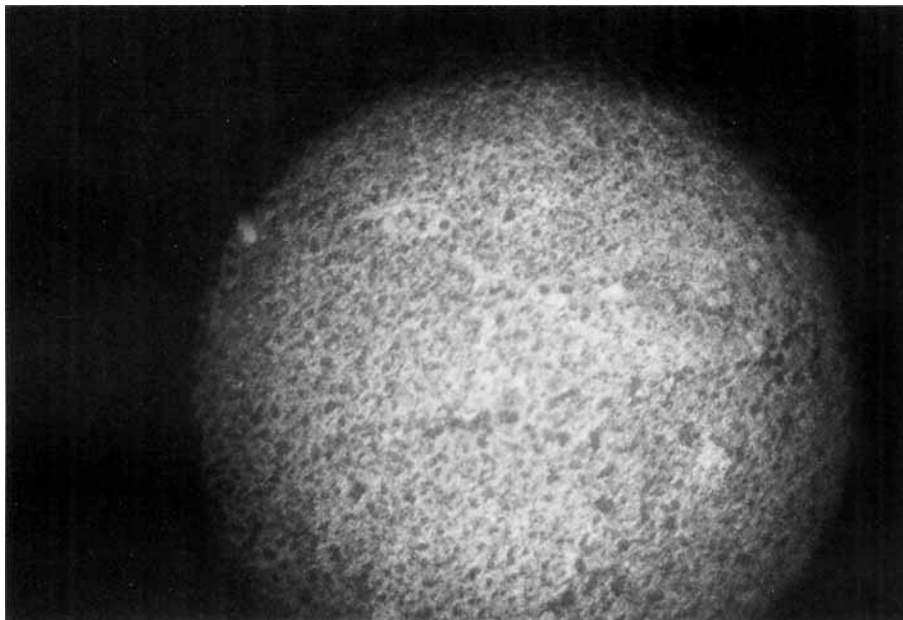


(D)

Figure 8 (Continued from the previous page)

PCL-CAB blend, for which spherulites increase slightly in size and show a more uniform shape after heating [Fig. 8(c)] than those without thermal treatment [Fig. 8(d)]. PCL morphology has been reported to be strongly dependent on thermal history and crystallization temperature,²⁵ and, therefore, we were unable to address these morphological changes at this level of CAB content. In contrast, isolated groups of small spherulites were observed in 50/50 blend (not showed here). These spherulites disap-

peared by heating up to 237°C and cooling back to room temperature. After annealing at 40°C for 12 h, a scarce number of dispersed, highly refringent axialites were shown for this blend. This trend of morphological changes was enhanced in the 25/75 blend, in which very irregular axialite was observed, and only three or four bright points were evident in the photomicrograph [Fig. 8(e)]. After thermal treatment, this blend exhibited only a scarce number of well-defined, grayish areas in a rather pale matrix



(E)

Figure 8 (Continued from the previous page)

(not showed here), and it was unable to develop spherulites after annealing at 40°C for 12 h. In short, it is evident that a high content of CAB causes quite a decrease in the number and size of PCL spherulites, and this effect is enhanced with thermal treatment. These microscopic observations qualitatively concur with results obtained from DSC, DMA, and WAXS experiments, supporting the finding of partial miscibility in PCL-CAB blends.

Transesterification reactions may take place between components in polyester blends at high temperature. In such a situation, miscibility would be favored, leading to misinterpretation when miscibility studies are based only on DSC and DMA measurements.²⁶ For this reason, we used ¹³C-NMR spectroscopy to check whether transesterification occurs in these blends. This technique, among others,²⁶ has been proven useful for detecting this reaction in polymer blends. Thus, ¹³C-NMR spectra were obtained for pure polymers and blends containing 50 and 25% of PCL, before and after being thermally treated at the same conditions of DSC measurements (second run). Peaks in these spectra did not change either in position or in their relative heights. Spectra for the untreated, pure polymers and their blends were practically identical in shape to those of thermally treated samples. This can be appreciated in Figure 9, in which only representative spectra are shown: Those of untreated PCL and CAB, as well as of the thermally treated 25/75 PCL-CAB blend. At this point, it is worth mentioning

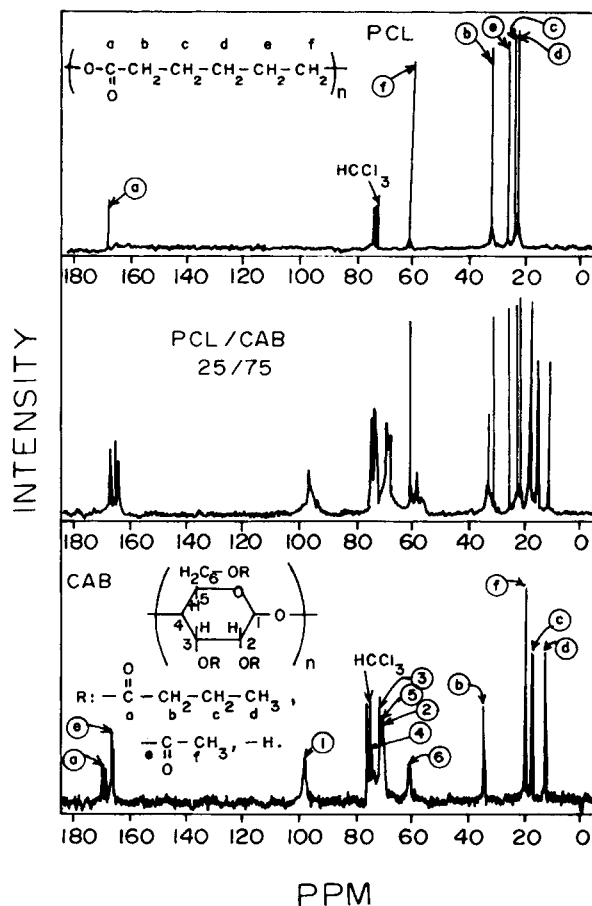


Figure 9 ¹³C-NMR spectra of pure PCL and CAB and of 25/75 PCL-CAB blend.

that the thermally treated blends were easily redissolved in dichloromethane and chloroform, without gel formation. Furthermore, it must be recalled that DSC traces of four successive runs performed on the 50/50% blend resulted identical to that of the second run. Endothermal peak decreased in size only after the fifth and subsequent runs. Thus, based on this observation and the lack of changes in the ^{13}C -NMR spectra, we can ensure that transesterification or decomposition did not take place in PCL-CAB system, at least up to the third DSC run. It must be recalled that the foregoing discussion on DSC results was based on the information obtained from the first and second runs. Therefore, the finding of partial miscibility for this system, based on DSC and DMA measurements, is of good confidence.

PCL-CDA Blends

Thermal behavior of these blends is similar to that of PCL-CAB blends in some features. This can be observed in Figure 10, where representative DSC traces for PCL-CDA blends are depicted. T_g for these blends was not clearly defined on the first DSC run, but it was apparent on the second run, like for PCL-CAB blends. It can be observed that T_g for PCL-CDA blends exhibits a slight variation, from 453 K for pure CDA to 440 K for 50/50 blend, and a wider temperature range than that for PCL-CAB.

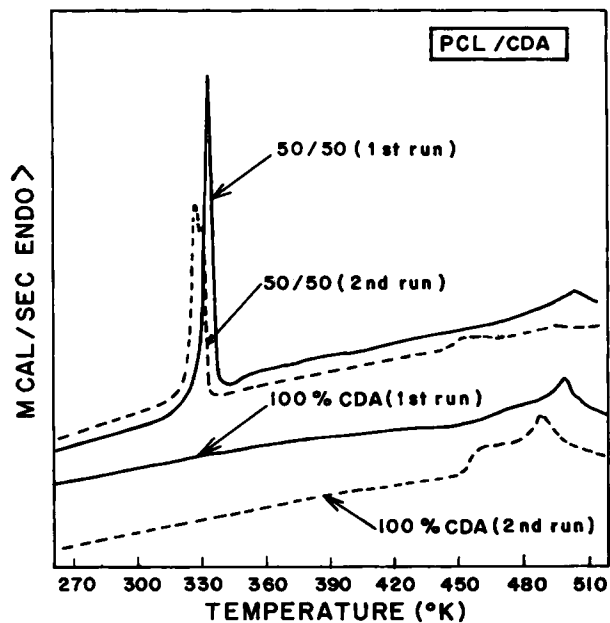


Figure 10 Representative DSC thermograms for PCL-CDA blends. Experimental conditions: $10^\circ\text{C}/\text{min}$ under a N_2 flux of $20\text{ cm}^3/\text{min}$.

Table II Glass Transition Temperature for PCL-CDA Blends from DSC Measurements

Blend Composition	Blend				
	0/100	10/90	25/75	50/50	60/40
$T_g, ^\circ\text{C}$	180	178	177	176	176

Though T_g for PCL was not evident in DSC thermograms, it is clear that the T_g value of CDA was independent on the PCL content (Table II). Then, with basis on the T_g criterion, we can conclude that this system is immiscible.

Regarding the melting behavior, the 50/50 blend exhibits also a depression for T_m , and a double-melting peak, though incipient, was distinguishable only after heating up to 237°C and cooling back to room temperature (Fig. 10). Thermal parameters for PCL-CDA blends decrease with the CDA content, as shown in Figure 11. These DSC curves for PCL-CDA closely resemble those for PCL-CAB, but the decrease in T_m and ΔH_f for CDA-rich blends was significantly lower than that observed for PCL-CAB.

On the other hand, X-ray crystallinity of PCL decreases markedly with the addition of CDA (Fig. 12 and the middle of Fig. 6), unlike the monotone decrease of this parameter observed on the thermally untreated PCL-CAB system (upper part of Fig. 6, continuous curve). Thermal treatment caused only a further, slight decrease in crystallinity for PCL-CDA system, as can be seen for 25/75 blend (Fig. 12) and for all the PCL-CDA blends (Fig. 6, dis-

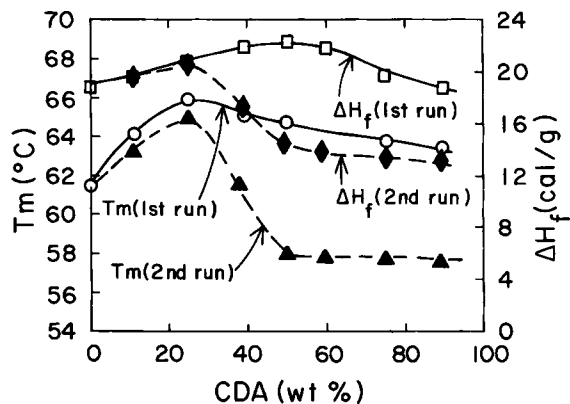


Figure 11 Thermal events for PCL-CDA blends as a function of composition. Melting temperature (T_m) on the (\ominus) first and the ($-\triangle-$) second DSC runs. Enthalpy of fusion (ΔH_f) for the (\boxplus) first and the ($-\diamond-$) second DSC runs.

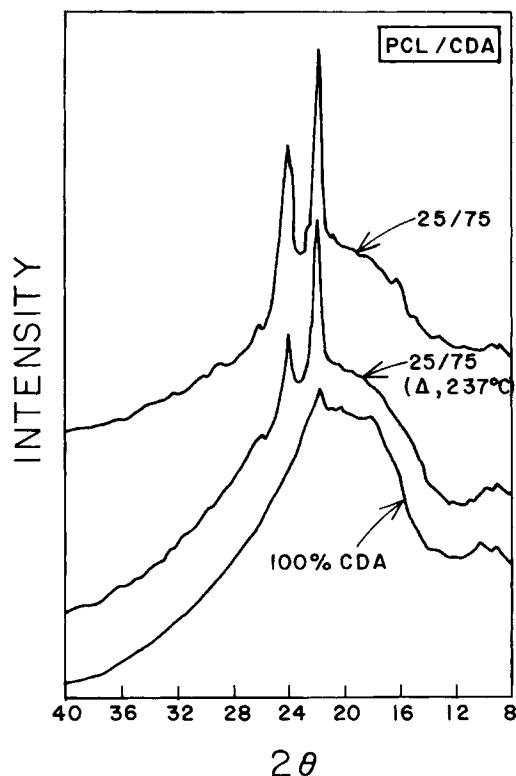
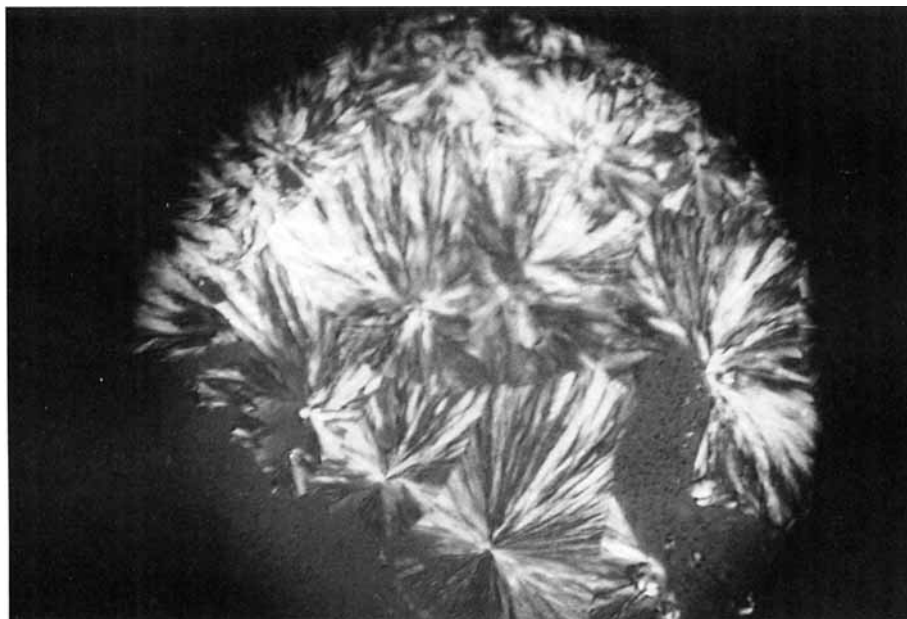


Figure 12 Representative WAXS diffractograms for the PCL-CDA blends. Numerals on curves indicate blend composition and (Δ , 237°C) means that the sample was heated and cooled back.

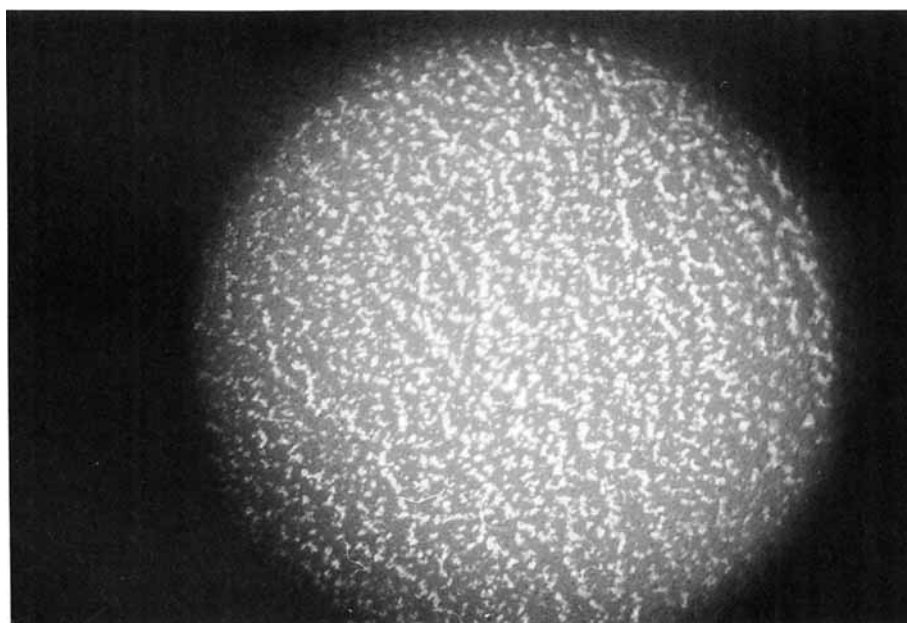
continuous curve at the center). This behavior contrasts with the drastic decrease in crystallinity observed for the thermally treated PCL-CAB blends. These results concur qualitatively with those of optical microscopy. Thus, spherulites shown up by the as-cast blend containing 25 wt % of CDA were distributed more or less uniformly in the whole sample [Fig. 13(a)], but they became highly impinged after heating up to 237°C and cooling back to room temperature [Fig. 13(b)]. Also, white zones in this figure (presumably cumulated small crystallites) became grayish and almost free of spherulites, which concurs with the decrease of its crystallinity index after thermal treatment. However, when this thermally treated sample was annealed at 40°C for 12 h, an appreciable number of very small spherulites appeared in these grayish zones. Then, it seems that CDA only disperses PCL and restrains the spherulites size. This effect can be more clearly appreciated in the photomicrograph of the as-cast 25/75 blend [Fig. 13(c)], in which small, highly dispersed propellant-shape axialites are shown. These axialites practically disappeared after being thermally treated. However, after a period of 24 h at room temperature, bright colored points (presumably rather small axialites) developed also in this blend, like in the PCL-rich blends. Then, in an attempt to induce these axialites to enlarge, annealing was applied on the blend at 40°C for 12 h, resulting in a



Figure 13 Polarized photomicrograph for PCL-CDA blends: (a) As-cast and (b) thermally treated 75/25 blend; as-cast 25/75 PCL-CDA blend.



(B)



(C)

Figure 13 (Continued from the previous page)

significant increase in the number of axialites, though their size remained practically unchanged. Based on this observation and the foregoing results, it can be assumed that CDA disperses PCL and, therefore, restrains and retards the primary crystallization process of PCL. This can be understood by recalling that temperature crystallization of PCL is rather below the T_g of CDA, which implies that PCL is immersed in a rigid, glass matrix of CDA. Also, it is possible that a very weak interaction takes

place at the interfaces between both components in this system.

PCL-CTA Blends

This system shows a very interesting behavior as compared with the foregoing systems. (i) DSC traces do not exhibit a clearly defined T_g in either the first runs or the second runs (Fig. 14) and, therefore, we are unable to conclude about miscibility of this sys-

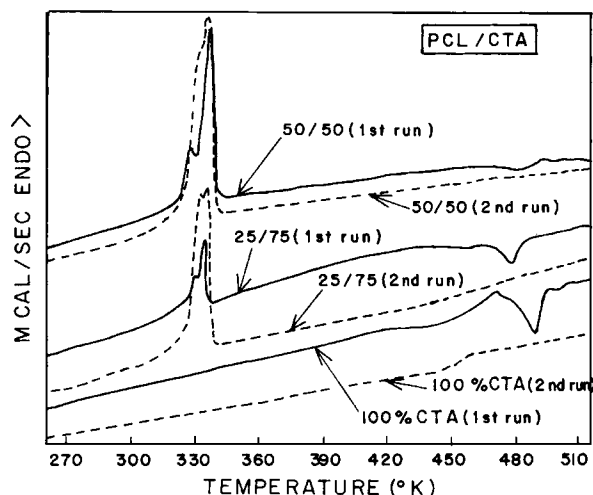


Figure 14 Representative DSC traces for PCL-CTA blends. Experimental conditions: $10^{\circ}\text{C}/\text{min}$. under a N_2 flux of $20\text{ cm}^3/\text{min}$.

tem with basis on DSC results. (ii) Regarding the double-melting peak, which is also shown by this system, the peak of lower T_m is smaller than that of higher T_m (Fig. 14), whereas the reciprocal is true for PCL-CAB. (iii) A strong decrease on both the ΔH_f and the T_m with the addition of CTA was observed for the as-cast blends (Figs. 14 and 15), in contrast to blends containing CDA or CAB. Furthermore, these parameters increased in value on the second DSC run, i.e., after being heated up to about 237°C (Fig. 15). Such a behavior is quite contrasting with that observed for the other two systems studied here. An additional thermal event exhibited

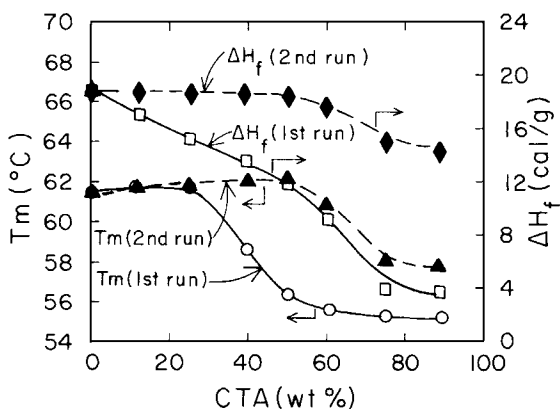


Figure 15 Thermal events for PCL-CTA blends as a function of composition. Melting temperature (T_m) for the (○) first and the (—▲—) second DSC runs. Enthalpy of fusion (ΔH_f) for the (□) first and the (—◆—) second DSC runs.

by PCL-CTA is an exotherm of crystallization by heating, which is a characteristic of CTA. Although this phenomenon is not often observed in polymers, a discussion was not elaborated on because this exothermal peak did not vary significantly with blend composition.

Figure 16(a)–(c) reports data of dynamic mechanical measurements for PCL-CTA blends. It is quite evident in this figure that T_{α} of CTA at 205°C [Fig. 16(a)] remains near this value when blended with PCL [Fig. 16(b)], which occurs even for PCL-rich blends [Fig. 16(c)]. The T_{α} of PCL is not evident in the 40/60% PCL-CTA blend, but it appeared at about -25°C in the 60/40% blend [Fig. 16(c)]. In this figure, a peak at 65°C due to melting of crystalline phase of PCL is also shown. Since T_{α} of CTA does not depend on composition of PCL, it can be concluded that PCL-CTA blends are immiscible.

Enthalpy behavior of PCL-CTA blends concurs with those obtained by WAXS. As can be seen in Figures 17 and 18, apparent crystallinity of PCL

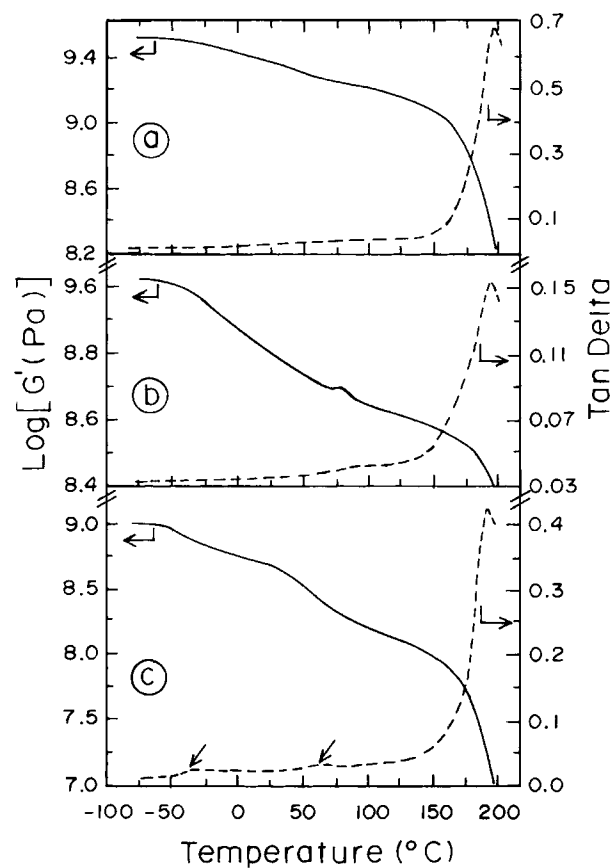


Figure 16 (—) Shear modulus G' and (---) tan delta from dynamic mechanical measurements: (a) Pure CTA, (b) 40/60 PCL-CTA, and (c) 60/40 PCL-CTA.

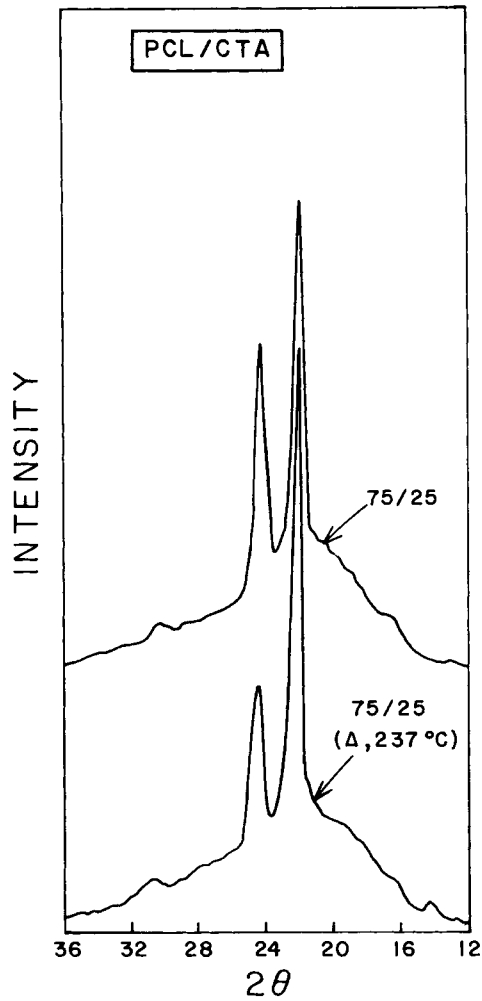


Figure 17 WAXS diffractograms for the as-cast and thermally treated 75/25 PCL-CTA blend.

decreased with the CTA content, but this crystallinity increased after thermal treatment. This thermal effect can be more clearly observed on diffractograms for the 50/50 blend. The two peaks at 2θ of 21.6° and 24.2° (scattering of PCL crystals) are comparable in height before heating. However, after heating and cooling back, an increase on intensity was observed for the peak at $2\theta = 21.6^\circ$, and a decrease for that at $2\theta = 24.2^\circ$ (Fig. 18), unlike the PCL-CAB blends. This later diffractogram, which was obtained for the thermally treated sample, resembles more closely that of pure PCL, rather than that of the as-cast sample. This gives an indication that heating causes a partial recovering of the original morphological aspects. Nevertheless, the apparent crystallinity of PCL was actually affected by the presence of CTA, in both the thermally treated samples and the as-cast blends, as can be clearly

observed in Figure 6 (bottom part, continuous and discontinuous curves).

On the other hand, optical microscopy brought out a great population of very small spherulites in the 75/25 PCL-CTA blend [Fig. 19(a)], which did not show an appreciable change after thermally treated [Fig. 19(b)]. In contrast, the great population of axialites observed on the 25/75 blend [Fig. 19(c)] became clearly birefringent, white matrix after heating [Fig. 19(d)]. This white matrix contains a small fraction of dark zones that can be a heterogeneous mixture of amorphous components. With basis on the fact that small spherulites grew significantly in number on this later blend under annealing at 40°C for 12 h, one can assume that crystallinity of PCL was recovered, at least in part, after annealing. This assumption is in qualitative accordance with the observed percent of apparent crystallinity for the same blends in Figure 6 (bottom part, discontinuous curve), which shows only a slight

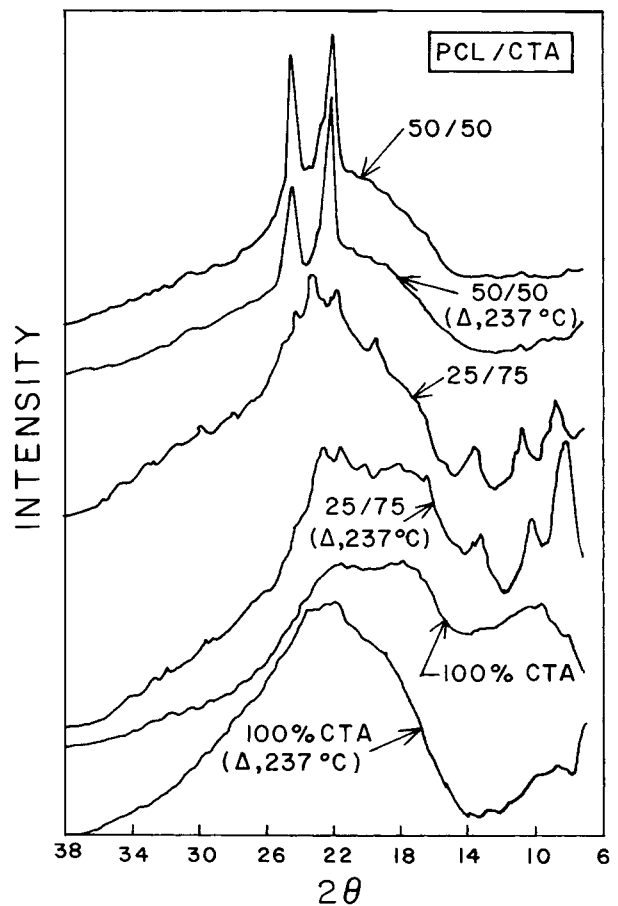


Figure 18 WAXS diffractograms for the as-cast and thermally treated PCL-CTA blends. Numerals on curves indicate blend composition.

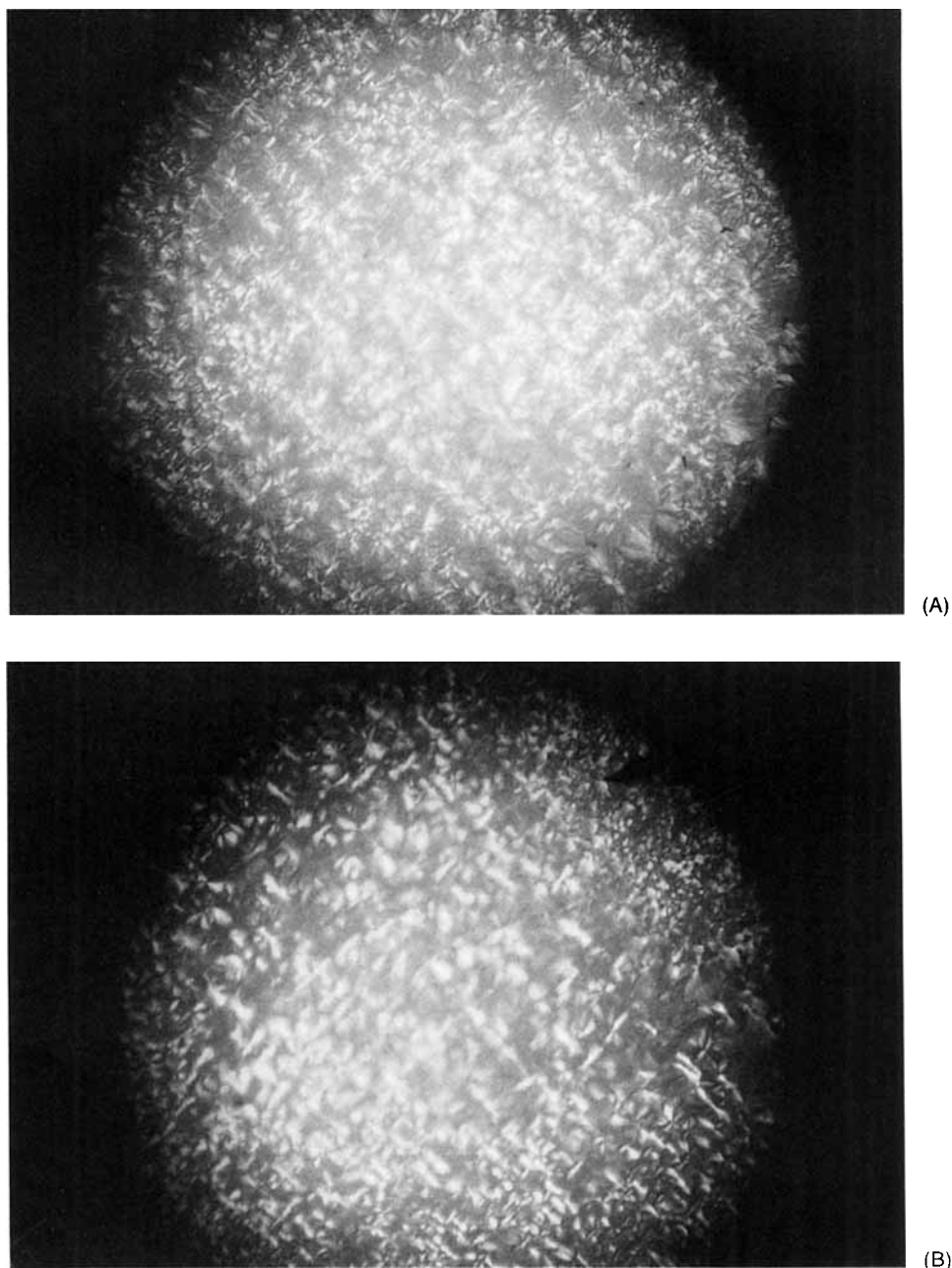
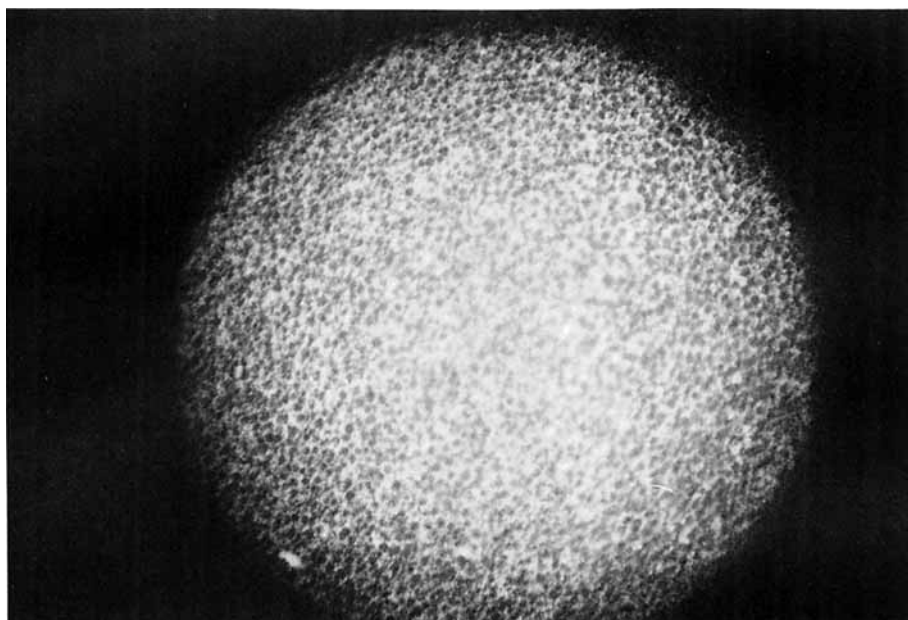


Figure 19 Polarized photomicrograph for the PCL-CTA blends: (a) as-cast and (b) thermally treated 75/25 (PCL-CTA) blend; (c) as-cast and (d) thermally treated 25/75 PCL-CTA blend.

negative deviation from the additivity rule in crystallinity index. Also, this concurs qualitatively with the immiscibility determined by DMA.

It is worth mentioning that a hexagonal, regular structure was formed on PCL blends containing 75% of CDA, after solvent was allowed to evaporate at 36°C (Fig. 20). This structure was apparent only under POM, covering entirely the as-cast films and

resembling a honeycomb net-work. A similar structure was also observed on PCL-CTA blends containing 75% of CTA, though hexagons was not as well defined in this blend as in PCL-CDA. This phenomenon, also with lower definition, has been reported elsewhere²⁷ when studying the phase separation occurring on cast blends of cellulose with synthetic polymers. Interesting, this structure did



(C)



(D)

Figure 19 (Continued from the previous page)

not appear in PCL-CAB blends when subjected to the same conditions, probably due to the partial miscibility of this system. Kinetic studies of this interesting phenomenon is in progress at present by digitalizing images and polarizing optical microscopy.

From the above discussion, it seems to be adequate to compare the thermal behavior as well as the X-ray crystallinity shown by the three systems after thermal treatment. This information is con-

tained in the DSC curves (second runs) and in X-ray diffractograms, labeled as (Δ , 237°C), in Figures 3, 6, 11, 12, 16, and 18. Then, after inspection of such curves, it is evident that thermal behavior of PCL-CDA blends is similar to that of PCL-CTA blends, with both systems exhibiting immiscibility, whereas PCL-CAB is partially miscible. This finding leads to the assumption that there exists a complex interaction between the hydroxyl and carbonyl groups in these systems. At this point, it should be

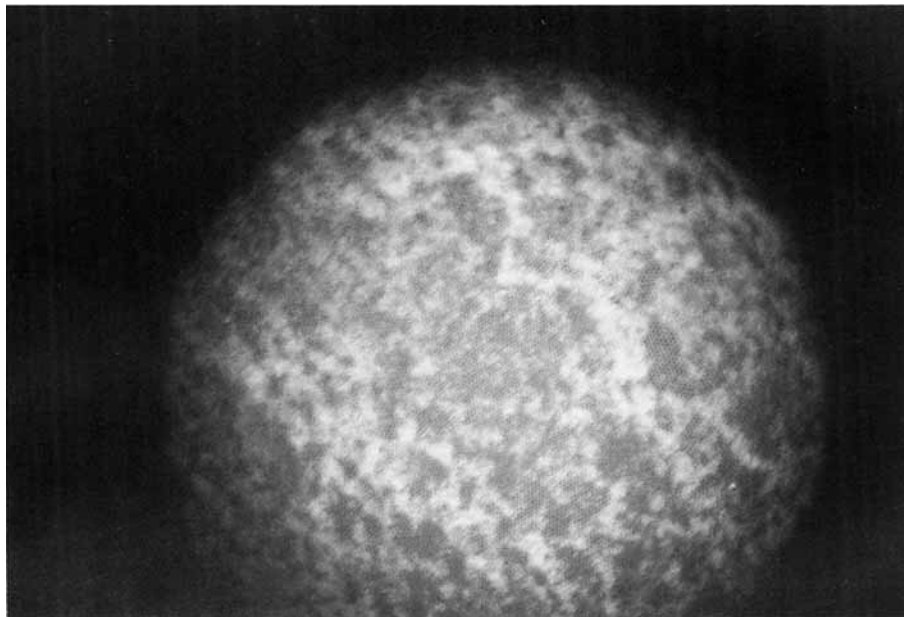


Figure 20 Polarized photomicrograph for the 25/75 PCL-CDA blend after cast at 36°C. An hexagonal structure resembling a honeycomb network can be appreciated on the surface.

emphasized that the used CAB has an intermediate ratio of hydroxyl groups to repeating unit, lying between those of CDA and CTA, according to the sequence 0.01 for CTA < 0.2 for CAB < 1.0 for CDA. Obviously, this sequence does not correspond to the order of miscibility state shown by the CDs used here. Due to the structural complexity of these polymers, conformational studies are required to understand blend miscibility in a deeper level. Therefore, considering the reported conformation for cellulose²⁸ and cellulose triacetate,²⁹⁻³¹ one can reasonably assume that all the nonsubstituted hydroxyl groups are staggered in position in CDA as well as in CAB, when viewed through the polymer chain axes from one extreme to the other. As the degree of substitution is higher in CAB than in CDA, these hydroxyl groups are necessarily much more separated in CAB than in CDA, and this might favor the highly flexible chains of PCL to accommodate in a more interacting configuration with CAB than with CDA. Nevertheless, more studies on the conformation and morphology of CDs, alone and blended, are necessary to understand the role of butyryl groups on the interaction of CAB with PCL.

CONCLUSIONS

Thermal behavior in DSC as well as the extent of crystallinity of binary cast blends involving PCL

with CAB, CDA, and CTA clearly showed a solvent effect. After heating and cooling back, such an effect was no longer evident, which allows us to compare appropriately the behavior shown by these three systems. On the basis of DSC and DMA characterization, the PCL-CAB system is partially miscible in the CAB-rich region of composition. This is reinforced by the drastic decrease on both crystallinity index and ΔH_f , as well as on T_m as the CAB content was increased. Results of POM concur qualitatively with this observation. Furthermore, ¹³C-NMR spectroscopy indicates that PCL, CAB, and their blends did not suffer transesterification or decomposition, at least up to the fourth DSC run. PCL-CDA and PCL-CTA blends showed, in turn, to be immiscible, unlike PCL-CAB blends. Despite of this immiscibility, crystallinity index and ΔH_f , as well as the thermal parameter T_m , decrease with the CDA (or CTA) content, which can be associated with the restriction imposed by the glassy matrix CDA on PCL crystallization. On the other hand, the double-melting behavior shown by PCL-CAB seems to be associated with two populations of crystals, because peaks position is independent on the heating rate of DSC runs. Nevertheless, additional studies are necessary to quantify the morphological effect of cellulosics on PCL.

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